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Produced by the NASA Center for Aerospace Information (CASI)
Final Report: Bimetallic Treatment System (BTS) for Removal and Remediation of Polychlorinated Biphenyl from Marshall Space Flight Center’s 4696 F1 Stand

Funded by Office of Space Flight

OBJECTIVE

This OSF-funded project sought to demonstrate the application of a Bi-metallic Treatment System (BTS) to remove and degrade PCBs found on NASA facilities. The project initiated with the collection of PCB-containing materials from various MSFC and KSC structures, followed by laboratory evaluation of the BTS’ PCB-removal efficiency, and concluded with a field demonstration at MSFC. The project evaluated the optimum formulation required to remove PCBs from aged and weathered paint with the goal of achieving final PCB concentrations less than 50 mg/Kg or 50 percent reduction where PCB starting levels were already below the 50 mg/Kg levels. Using lessons learned from this study, it was anticipated that the research team would be better able to make further recommendation on application strategies for future use of BTS for the treatment of PCB laden coatings on structures.

PROBLEM STATEMENT

Numerous NASA facilities have older metal structures upon which paints containing polychlorinated biphenyls (PCB) were applied. These painted structures may pose worker and ecological health hazards and if planned for disposal, are considered a TSCA-level (Toxic Substance Control Act) waste. Some of the affected structures could be refurbished and utilized for new programs, but because the paint currently on the structures is heavily laden with PCBs, NASA may be unable to reuse or even discard these structures without significant cost. The research described in this report details the field-scale deployment of a new and innovative solution for the removal and destruction of PCBs found in painted structures or within the binding or caulking material on structures. The technology incorporates a Bimetallic Treatment System (BTS) that extracts and degrades only the PCBs from painted facilities, leaving the structure virtually unaltered.

In 2003, NASA Kennedy Space Center (KSC) began investigating the potential of using a solvent-based system to remove PCBs found in paints located on a number of structures at three of their operating Centers. This innovative research was initially funded by NASA’s Environmental Program Office and KSC’s Center Director Discretionary Fund, with follow-on funding provided by NASA’s Office of Space Flight. The funding included the preliminary proof of concept laboratory research and the demonstration of BTS on parts set aside from NASA’s Launch Umbilical Tower at KSC. Additionally, main engine test stands at Marshall Space Flight Center (MSFC) were tested for PCB removal and destruction using BTS. Both of these structures were utilized during the Apollo Program and the test stands at MSFC could potentially be reutilized by NASA for its future launch vehicle testing.
INTRODUCTION

Polychlorinated biphenyls (PCBs) are a group of synthetic aromatic compounds with the general formula $C_{12}H_{10-x}Cl_x$ that were historically used in industrial paints, caulking material and adhesives, as their properties enhanced structural integrity, reduced flammability and boosted antifungal properties. Although the United States Environmental Protection Agency (USEPA) has banned the manufacture of PCBs since 1979, they have been found in at least 500 of the 1,598 National Priorities List (Superfund) sites identified by the USEPA. Prior to the USEPA’s ban on PCB production, PCBs were commonly used as additives in paints and asphalt-based adhesives that were subsequently applied to a variety of structures. Government facilities constructed as early as 1930 utilized PCB-containing binders or PCB-containing paints, which are now leaching into the environment and posing ecological and worker health concerns. To date, no definitive in situ, non-destructive method is available for the removal of PCBs found in weathered coatings or on painted structures/equipment.

In 2003, researchers at the Kennedy Space Center and the University of Central Florida began investigating the potential of using a solvent-based treatment system to remove PCBs found in paints located on a number of structures at three NASA Centers. This research led to the development of a Bimetallic Treatment System (BTS) comprised of elemental magnesium (Mg) particles enriched with a small number of catalytic palladium (Pd) sites that are utilized in conjunction with a solvent system. The solvent is capable of reacting with Mg/Pd to produce the hydrogen atoms that are required to complete the hydrodehalogenation reaction cycle for PCBs. BTS technology has two functions: first, to extract the PCBs from weathered, decades-old coating material, such as paint; and second, to degrade the extracted PCBs to nonhalogenated by-products. Figure 1 represents the pictorial architecture of BTS with a photograph below showing application of BTS to a vertical wall.

This report introduces BTS formulations that are capable of extracting PCBs in situ from painted structures. The final results achieved at MSFC will be presented along with statistical interpretation of the data generated.

MATERIALS AND METHODS

BTS’ removal and degradation of PCBs occurs via two independent processes; the chemical extraction of the PCBs from the structure and the PCB’s subsequent destruction in the presence of the catalyst system. BTS’ goal is to extract PCBs without destroying the paint and partition them into an environmentally friendly solvent. Our research indicates this can usually be accomplished within 24-72 hours of BTS contact. PCBs are extremely hydrophobic and prefer to be in the BTS instead of in hardened paint or binder material. The solvent is used to open, but not destroy the paint’s polymeric lattice structure, allowing pathways for PCB movement out of the paint and into the solvent. The solvent and reactive system containing the metal and proton donor are blended together along with thickening agents to create a paste-like product that can be applied to the PCB-laden surface. A number of solvent systems have been tested and are compatible within BTS. The lattice structure upon which BTS has been applied returns to its original configuration, with minimal change in surface appearance, texture, or hardness.
FIGURE 1. Pictorial Diagram (A) of a Bimetallic Treatment System and picture of application (B).

The catalyst system developed by the team is manufactured using a mechanical alloying method. It has been optimized for use in BTS and typically consists of 0.1% Pd on Mg (Aitken et al., 2006). Several experiments were run using the dry metal in aqueous PCB solutions to determine the catalyst to metal ratio. The Mg/Pd bimetal is a potent hydrogenation reagent capable of removing the chlorine from a high concentration solution of chlorocarbons in minutes (Engelmann, 2003). Literature suggests the degradation end-product for the dehalogenation of all Aroclor mixtures is the biphenyl ring, which is a benign end-product (Doyle, 1998).
Magnesium metal, a powerful reducing agent, reacts with water to form hydrogen gas ($H_2$) and magnesium hydroxide (Brown et al., 2005). Palladium is a well-documented hydrogenation catalyst that chemisorbs molecular hydrogen, weakening the bond between the hydrogen atoms, forming atomic hydrogen bound to the palladium surface (McMurray, 2000) and (Tsuji, 2004). It is hypothesized that the interaction of the bimetallic Mg/Pd system with a solvent containing available hydrogen moieties (i.e. alcohols or water) results in the generation of atomic hydrogen at particular sites on the metal surface. The unbound, atomic hydrogen is available for reaction with PCB molecules that come into contact with the catalytic surface resulting in a reductive dehalogenation reaction. The proposed reaction mechanism is shown below:

$$Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2$$

$$H_2 (\text{Pd catalyst}) + RCl \rightarrow RH + HCl$$

Rapid and complete dechlorination of PCBs in aqueous/solvent systems in the presence of the catalyst system described above has been documented (Doyle, et al., 1998). Table 1 illustrates the typical degradation results achieved in an aqueous system comprised of water, 10% methanol, and the bimetal Mg/Pd. Methanol was added to the water to increase the solubility of PCBs in the stock solution. The samples were run via GC/MS using a modified version of EPA method 8270. Addition of the Mg/Pd particles to an aqueous system immediately begins to produce large amounts of hydrogen gas.

Due to safety concerns associated with the large production of hydrogen when the Mg/Pd was added to water, other potential solvents such as pure methanol and ethanol solutions were tested resulting in similar rates of PCB dehalogenation. The oxidation of the magnesium metal is not as exothermic when alcohols are substituted for water thus decreasing the likelihood of potential ignition of hydrogen gas. The solvents themselves carry flammability cautions that must be addressed in the field during BTS application using best management practices.

Additional BTS formulation properties that must be addressed for each site-specific application include viscosity and stability. The BTS must be viscous enough to remain where it is applied and several thickening agents have been tested. Adding a stabilizing agent ensures the BTS will not evaporate and leave the unprotected Mg/Pd exposed. Due to the extreme reactivity of BTS, the choice of thickening and stabilizing agents is complex. During BTS formulation testing, a number of reagents were evaluated to ensure the rate of dehalogenation was not inhibited by its addition to the system.

Combining the optimal solvent catalyst system, thickeners and stabilizing agents forms a paste-like BTS system. As stated earlier, each structure requires specific formulation optimization to ensure success. For example, the launch umbilical tower (LUT) for the retired Apollo program required the use of toluene or d-limonene as a solvent to soften the paint to allow PCB migration. For experiments with this structure, we applied specific paste formulations to sample structures and compared analytical results pre- and post-application of
Analyses of these samples is quite complex. We have found that most structures have varying levels of PCBs by weight percent on the same structure. This may be due to weathering of the paints or variations in the paint thickness.

A field deployment of several BTS formulations and application strategies were tested on the inside of a retired engine test stand at Marshal Space Flight Center (MSFC) in Huntsville, Alabama. The objective of this field deployment was to transition laboratory generated results to a real-world setting to determine the effectiveness of the BTS, and to optimize application procedures. Figure 2 is a picture of the BTS application site at MSFC.

FIGURE 2. Site MSFC 4696.
Using lessons learned from laboratory testing on both LUT panels and MSFC paint chips, the research team decided to try several BTS formulations, application procedures and exposure durations at MSFC. The location for the different formulation placements are detailed in Figure 3, along with a legend indicating which formulations were used at each location. Several different batches of BTS were deployed and each batch was made as either an active BTS or inactive BTS mix (See Table 1). Active refers to the presence of the palladium catalyst in the formulation, and inactive indicates a lack of this material (used microscale iron (Fe) instead of Mg/Pd). For the MSFC deployment, five one-gallon drums were made of both inactive toluene-based BTS and inactive limonene-based BTS. Additionally, one gallon of active limonene-based BTS, one gallon of active toluene-based BTS and one gallon of no-metal BTS were made.

Also during the MSFC deployment, a series of BTS application methods were tested using active BTS systems. The unique application methods were termed “band-aid”- type systems. With this method, instead of directly wiping BTS directly onto the metal surface, the material was placed between a fabric and a backing material; much like a cotton band-aid strip sits upon an adhesive bandage. The fabrics tested were made from felt, cotton baby diaper pads, and t-shirt material. This application approach was tested to address the potential of adding BTS to non-horizontal surfaces.

**TABLE 1. Formulations of BTS paste systems for the field study at MSFC.**

<table>
<thead>
<tr>
<th>BTS Formulation</th>
<th>Solvent, Volume (ml)</th>
<th>Metal, Wt. (g)</th>
<th>Thickener/Stabilizer, Wt. (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Limonene Inactive</td>
<td>Limonene (10%) in ethanol, 110 ml</td>
<td>Iron, 20 g</td>
<td>Glycerin, 20 g</td>
</tr>
<tr>
<td>Toluene Inactive</td>
<td>Toluene (10%) in Ethanol, 111 ml</td>
<td>Iron, 20 g</td>
<td>Calcium Stearate, 20 g</td>
</tr>
<tr>
<td>Limonene Active</td>
<td>Limonene(10%) in ethanol, 153 ml</td>
<td>Mg-Pd, 20 g</td>
<td>Glycerin, 20 g</td>
</tr>
<tr>
<td>Toluene Active</td>
<td>Toluene (10%) in Ethanol, 153 ml</td>
<td>Mg-Pd, 20 g</td>
<td>Calcium Stearate, 20 g</td>
</tr>
<tr>
<td>Limonene No Metal</td>
<td>Limonene (10%) in ethanol, 144 ml</td>
<td>None</td>
<td>Calcium Stearate, 20 g</td>
</tr>
</tbody>
</table>

All inactive formulations contained iron and no palladized magnesium. The purpose for making these formulations was to determine the efficiency of the BTS to remove PCBs from the structure when no catalyst was present for the subsequent degradation step. If these “inactive” systems were effective at removing PCBs, future systems could be deployed that simply removed PCBs from the building in some independent step from the degradation step, which then could be “activated” for PCB reduction at a different time and/or location. Considering the
expense and potential safety hazards associated with the use of palladized magnesium, a viable multi-step application process may prove to be valuable. Iron was chosen as the replacement metal to magnesium because of its low cost and availability. The iron’s presence notably slowed down ethanol’s volatilization as compared to no metal-containing paste formulations.

**Test panels indicate type of solvent system used and exposure duration. Only panels I and J had active catalyst systems containing Mg/Pd applied to them. The remaining panels used micron-sized iron only or no metal at all.**

**FIGURE 3. Site Mapping of BTS Application at MSFC 4696.**
FIGURE 4. Photograph of BTS test panels covered with aluminum foil or copper sheets.

Paint samples were analyzed prior to and post treatment with BTS. The samples were scraped off the structure and collected in plastic baggies. In the laboratory, these samples were homogenized using a mortar and pestle. The iron shavings from the structure that were scraped along with paint were removed from the sample with the use of a magnet. The remaining scraped paint residue was soaked in a small amount of toluene for approximately one hour to aid in softening the paint, before an additional volume of 5 ml of ethanol was added. The samples were then sonicated using a high energy, sonic dismembrator for 3.0 minutes. This method is similar to EPA SW 846 Method 3500B. At this point, 2 ml of deionized water were added to each sample followed by 5.0 ml of hexane. The samples were then shaken vigorously for 2.0 minutes and centrifuged. The top hexane layer was analyzed for PCBs via GC/MS similar to EPA SW-846 Method 8082B. The purpose of the addition of the water was to make the ethanol layer more polar so that the non-polar PCBs would prefer the nonpolar hexane layer. Ethanol was used as an extraction solvent because of its ability to remove PCBs from the paint while holding onto the more polar interferences in the sample. Contaminants removed using this extraction included hexadecanoic acid and other fatty acids which originally interfered with analytical quantitation.
RESULTS AND DISCUSSION

The results in Tables 2 and 3 show that the degradation of PCBs can be achieved rapidly and completely in the presence of the catalyst system developed by the project team. The PCBs were rapidly degraded into nonchlorinated by-products as can be seen in Figure 4. The results in Table 3 demonstrate that the dechlorination process can take place without the presence of water. The suspected reaction in non-aqueous conditions involves utilizing the slightly acidic proton on the alcohols as the hydrogen that is replacing the chlorines in the dechlorination reaction. Future experiments testing this hypothesis will include the use of deuterated alcohols to track the potential movement of the hydrogen from the alcohols.

By-products formed from the reduction reaction are similar for both reactions; with water and without water. The data obtained from snapshots of the reaction show that the dechlorination process does occur somewhat stepwise. This is evident by the formation of lower molecular weight chlorinated biphenyls, signified by the earlier retention times that were not present in the same ratio in the untreated 100 mg/l PCB 1254 sample. Note the changing ratios of later eluting peaks in Figure 4. Additional by-products that may also be produced are lower molecular weight hydrocarbons. These compounds would be masked within the solvent peak if analyzed under typical PCB methods such as EPA method 8270. Future experiments will be conducted using headspace extraction to better characterize the presence of more volatile by-products. The by-products formed and the potential mechanisms of the dehalogenation reaction will be discussed in future publications.

### TABLE 2. Exposure of standard aroclor 1260 in 10% methanol in water solution to 1.0 g Mg/Pd.

<table>
<thead>
<tr>
<th>Sample Identification</th>
<th>Aroclor 1260 (mg/l)</th>
<th>% PCB Degradation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extracted Standard (no Mg/Pd)</td>
<td>5.9</td>
<td>0</td>
</tr>
<tr>
<td>5.9 mg/L Initial Concentration</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Standard exposed to Mg/Pd 1.0 hr</td>
<td>0.4</td>
<td>92 %</td>
</tr>
<tr>
<td>Standard exposed to Mg/Pd 4.0 hr</td>
<td>&lt;0.1</td>
<td>&gt;98 %</td>
</tr>
<tr>
<td>Standard exposed to Mg/Pd 4.0 hr (dup)</td>
<td>&lt;0.1</td>
<td>&gt;98 %</td>
</tr>
</tbody>
</table>

### TABLE 3. Exposure of standard aroclor 1254 in methanol only to 0.5 g Mg/Pd.

<table>
<thead>
<tr>
<th>Sample Identification</th>
<th>Aroclor 1254 (mg/l)</th>
<th>% PCB Degradation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extracted Standard (no Mg/Pd)</td>
<td>5.5</td>
<td>0</td>
</tr>
<tr>
<td>5.5 mg/L Initial Concentration</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Standard exposed to Mg/Pd 0.5 hr</td>
<td>0.3</td>
<td>95 %</td>
</tr>
<tr>
<td>Standard exposed to Mg/Pd 1.0 hr</td>
<td>&lt;0.1</td>
<td>&gt;98 %</td>
</tr>
<tr>
<td>Standard exposed to Mg/Pd 2.0 hr</td>
<td>&lt;0.1</td>
<td>&gt;98 %</td>
</tr>
<tr>
<td>Standard exposed to Mg/Pd 4.0 hr</td>
<td>&lt;0.1</td>
<td>&gt;98 %</td>
</tr>
</tbody>
</table>
The data represented in Table 4 demonstrates that the addition of glycerin as a thickening and stabilizing agent does not alter the efficacy of the catalyst to degrade PCBS. Other thickening agents such as starch and calcium stearate were also tested and produced similar results.

**TABLE 4. Exposure of standard aroclor 1260 in ethanol solution with and without the addition of glycerin.**

<table>
<thead>
<tr>
<th>Sample Identification</th>
<th>Aroclor 1260 (mg/l)</th>
<th>% PCB Degradation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extracted Standard (no Mg/Pd) 10.6 mg/L Initial Concentration</td>
<td>10.6</td>
<td>0</td>
</tr>
<tr>
<td>Standard exposed to Mg/Pd 24 hr</td>
<td>&lt;0.1</td>
<td>&gt;99 %</td>
</tr>
<tr>
<td>Standard exposed to Mg/Pd with glycerin 24 hr</td>
<td>&lt;0.1</td>
<td>&gt;99 %</td>
</tr>
</tbody>
</table>

Once the BTS formulations were optimized by choosing the most appropriate solvents, catalyst system, thickener and stabilizers, the system was tested on real world samples. Table 5 represents typical data obtained from applying the BTS to structures at Kennedy Space Center. Note the final concentrations of PCBs were well below the action level of 50 mg/Kg.

**TABLE 5. Launch umbilical tower (LUT) paint chips treated with BTS paste consisting of Mg/Pd, glycerin and methanol. Exposure time 24 hrs.**

<table>
<thead>
<tr>
<th>Sample Identification</th>
<th>Initial Concentration Aroclor 1260 (mg/Kg)</th>
<th>After BTS Aroclor 1260 (mg/Kg)</th>
<th>% PCB Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>LUT A Green 05/11/05</td>
<td>110</td>
<td>0.8</td>
<td>&gt;99 %</td>
</tr>
<tr>
<td>LUT A Green 05/18/05</td>
<td>260</td>
<td>9.7</td>
<td>96 %</td>
</tr>
<tr>
<td>LUT Red 05/18/05</td>
<td>7.7</td>
<td>0.2</td>
<td>97 %</td>
</tr>
</tbody>
</table>
FIGURE 4. Total ion chromatograms showing differing peak ratios of a 100mg/l Solution before and after treatment with Mg/Pd. Exposure time four hours.

For the MSFC field projects, structural samples were not available to be tested in the laboratory prior to outdoor application. The laboratory experiments required the use of limited samples (weathered paint chips only) to determine approximate concentrations before and after application of the BTS. Tables 6 and 7 exhibit the lab and field data obtained from using BTS at MSFC. The initial concentrations of PCBs within the paint are over an order of magnitude lower than the 50 mg/kg action level established by the EPA, making this site far from an ideal location to test the applicability of BTS for the remediation of PCB in painted structures. However, this data does show the wide range of applicability of BTS systems to paints with relatively low levels of PCBs (e.g. MSFC test stand with concentrations below conventional action level) to paints containing extremely high levels of PCBs (e.g. KSC’s Launch Umbilical Tower).
TABLE 6. Initial laboratory testing of Marshall Space Flight Center paint chips treated with BTS paste consisting of Mg/Pd, glycerin and ethanol. Exposure time of 24 hrs.

<table>
<thead>
<tr>
<th>Sample Identification</th>
<th>Initial Concentration Aroclor 1260 (mg/Kg)</th>
<th>After BTS Aroclor 1260 (mg/Kg)</th>
<th>% PCB Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>4696 F1 Stand</td>
<td>4.6</td>
<td>0.8</td>
<td>83 %</td>
</tr>
<tr>
<td>4553 F1 Stand</td>
<td>6.3</td>
<td>&lt;0.3</td>
<td>95 %</td>
</tr>
</tbody>
</table>

TABLE 7. Field results using a limonene-based BTS paste at MSFC building 4696 F1 stand.

<table>
<thead>
<tr>
<th>Time of Exposure (hr)</th>
<th>Initial Concentration Aroclor 1254 (mg/Kg)</th>
<th>Concentration Post-BTS Application Aroclor 1254 (mg/Kg)</th>
<th>% PCB Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>8 Panel F</td>
<td>3.46</td>
<td>2.65</td>
<td>23%</td>
</tr>
<tr>
<td>8 dup Panel F</td>
<td>3.21</td>
<td>2.87</td>
<td>11%</td>
</tr>
<tr>
<td>24 Panel D</td>
<td>3.28</td>
<td>2.39</td>
<td>27%</td>
</tr>
<tr>
<td>24 dup Panel D</td>
<td>3.11</td>
<td>2.23</td>
<td>28%</td>
</tr>
<tr>
<td>30 Panel H</td>
<td>4.16</td>
<td>22.82</td>
<td>-66%**</td>
</tr>
<tr>
<td>72 Panel B</td>
<td>4.18</td>
<td>1.79</td>
<td>57%</td>
</tr>
<tr>
<td>72 dup Panel B</td>
<td>12.35</td>
<td>6.54</td>
<td>47%</td>
</tr>
<tr>
<td>72 Panel I</td>
<td>4.36</td>
<td>2.55</td>
<td>41%</td>
</tr>
<tr>
<td>72 Panel K</td>
<td>3.69</td>
<td>3.03</td>
<td>18%</td>
</tr>
<tr>
<td>72 dup Panel K</td>
<td>4.17</td>
<td>3.52</td>
<td>16%</td>
</tr>
<tr>
<td>72 Panel L*</td>
<td>3.53</td>
<td>1.80</td>
<td>49%</td>
</tr>
<tr>
<td>72 Panel M*</td>
<td>2.50</td>
<td>1.82</td>
<td>27%</td>
</tr>
<tr>
<td>72 Panel N*</td>
<td>3.05</td>
<td>1.65</td>
<td>46%</td>
</tr>
<tr>
<td>72 Panel O</td>
<td>3.55</td>
<td>2.12</td>
<td>40%</td>
</tr>
</tbody>
</table>

*Average of two pre-samples shown. Only one post-sample taken at these locations.

** Post-application sample revealed higher concentration of PCBs than pre-application sample. Statistical data outlier as determined by the Grubbs’ Test for Outliers at 95% Confidence (α=0.05).
TABLE 8. Field results using a Toluene-based BTS paste at MSFC building 4696 F1 stand.

<table>
<thead>
<tr>
<th>Time of Exposure (hr)</th>
<th>Initial Concentration Aroclor 1254 (mg/Kg)</th>
<th>Concentration Post-BTS Application Aroclor 1254 (mg/Kg)</th>
<th>% PCB Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>8 Panel C</td>
<td>2.89</td>
<td>1.24</td>
<td>57%</td>
</tr>
<tr>
<td>8 dup Panel C</td>
<td>3.28</td>
<td>2.24</td>
<td>32%</td>
</tr>
<tr>
<td>24 Panel E</td>
<td>3.63</td>
<td>2.61</td>
<td>28%</td>
</tr>
<tr>
<td>24 dup Panel E</td>
<td>3.34</td>
<td>2.43</td>
<td>27%</td>
</tr>
<tr>
<td>30 Panel A</td>
<td>2.64</td>
<td>7.51</td>
<td>-184%**</td>
</tr>
<tr>
<td>30 dup Panel A</td>
<td>5.16</td>
<td>4.26</td>
<td>17%</td>
</tr>
<tr>
<td>72 Panel G</td>
<td>4.65</td>
<td>4.44</td>
<td>4%</td>
</tr>
<tr>
<td>72 dup Panel G</td>
<td>10.44</td>
<td>17.15</td>
<td>-64%**</td>
</tr>
<tr>
<td>72 Panel P*</td>
<td>3.21</td>
<td>2.46</td>
<td>23%</td>
</tr>
<tr>
<td>72 Panel R*</td>
<td>4.31</td>
<td>2.8</td>
<td>35%</td>
</tr>
<tr>
<td>72 Panel S*</td>
<td>9.77</td>
<td>5.79</td>
<td>41%</td>
</tr>
</tbody>
</table>

*averages of two pre-samples shown. Only one post-sample taken for these locations.

** Post-application sample revealed higher concentration of PCBs than pre-application sample. Statistical data outlier as determined by the Grubbs' Test for Outliers at 95% Confidence (α=0.05).

In order to determine whether the reduction of PCBs achieved by the different formulations was significant, a Paired Differences Statistical t-Test was performed. This statistical tool was used to indicate whether the differences between the pre- and post-application sample values were significant at a 95 percent confidence level (α=0.05). The test was run in order to verify that the data observed was not random, and indeed did prove a reduction in PCB levels as a result of the application of BTS. Additionally, the single Panel H sample and the duplicate of Panel G were determined at a 90 percent confidence level (α=0.10) by the Q-test to be data outliers and were not inputted into the Paired Difference t-Test. Panel A, however, was not determined to be an outlier and is included in the calculations. The statistical output from the analysis is presented in Table 9, where a p value of 0.008 was calculated for an α=0.05, which indicates the differences in the pre- and post-samples were significant. In correlation, the absolute value of t-Stat well exceeds the t-Critical for both the one-tail and two-tail values for the sample size of 22, again indicating that the differences in the pre- and post-BTS application data are significant. Therefore, BTS was statistically verified to be effective at lowering overall PCB concentrations found within the weathered paint on the 4696 Fl Test Stand.

Statistical analyses on the percent reduction observed for the different formulations (d-limonene formulation-vs.-toluene formulation) were also performed. Specifically the Grubbs' Test for Data Outliers was performed at a confidence interval of 95 percent (α=0.05). Based upon this outlier test, values from Panel A, Panel G duplicate and H were removed before calculating the average percent reduction and standard deviations for the d-limonene and toluene-containing formulations. The calculated values indicate an average percent removal of 33 percent for the d-limonene-containing formulation with a standard deviation of 14. For the toluene-containing formulation, the average percent reduction was 29 percent with a standard deviation of 15. There were insufficient data points to make any correlation about the time of
application and the percent removal efficiency amongst the different formulations tested. This should be addressed in future work.

### Table 9. Statistical Data from Paired Differences Test.

<table>
<thead>
<tr>
<th></th>
<th>Post</th>
<th>Pre</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average</td>
<td>3.610608867</td>
<td>2.704351993</td>
</tr>
<tr>
<td>P(T&lt;=t) one-tail</td>
<td>0.00409157</td>
<td>0.00818314</td>
</tr>
<tr>
<td>df</td>
<td>21</td>
<td>21</td>
</tr>
<tr>
<td>Obs.</td>
<td>22</td>
<td>22</td>
</tr>
<tr>
<td>Pearson Corr</td>
<td>0.096652945</td>
<td></td>
</tr>
<tr>
<td>Hypothesized Mean Diff</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Variance</td>
<td>1.843508645</td>
<td>0.451921021</td>
</tr>
<tr>
<td>t Stat</td>
<td>-2.920103964</td>
<td></td>
</tr>
<tr>
<td>df</td>
<td>21</td>
<td></td>
</tr>
<tr>
<td>P(T&lt;=t) two-tail</td>
<td>0.008183141</td>
<td>2.079613837</td>
</tr>
<tr>
<td>df</td>
<td>21</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>0.451921021</td>
<td></td>
</tr>
<tr>
<td>G dup</td>
<td>2.704351993</td>
<td>3.610608867</td>
</tr>
<tr>
<td>H and G dup</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Due to the wide variety of structural properties associated with each particular PCB laden-paint, the choice of solvent(s) incorporated into BTS is specific to the paint being treated. Treatability tests run by the team have shown that solvent systems that work very well at softening and removing the PCBs found in one variety of paint can be ineffective when applied to another. Therefore, the final formulation of BTS must be determined in the laboratory, in treatability tests using paint samples from the proposed area prior to determining the final formulation of BTS to apply. A number of "standard formulations" have been developed to address paints that have weathered under different conditions and which contain varying percentages of PCBs. It is important to note that "softening" of the paint simply refers to opening the polymeric lattice structure of the paint and is not intended to imply that the paint softens to a degree that it can be wiped off the structure or that any other action must be taken because the paint is "softer". It can in fact remain on the structure after BTS application. The catalyst system may be reclaimed to recover the noble metal, Pd. The non-toxic BTS formulation may be applied using a "paint-on and wipe-off" process, that in the end leaves the structure PCB-free and virtually unaltered in physical form.

### CONCLUSIONS

The work completed under this OSF-funded research initiative resulted in further development and refinement of an innovative *in situ* PCB remediation technology that allows more cost-effective and expedited cleanup of NASA infrastructure. Current approaches available to remediate PCBs from infrastructure either do not exist or are extremely labor-
intensive and therefore cost-prohibitive. BTS has been identified as a promising alternative to remediate PCBs found in paints, adhesives and caulking materials. Given the PCB source sites requiring remediation at NASA facilities, successful development and transition of this technology is expected to easily repay the investment through expedited facility cleanup and closure as well as future pollution prevention.

Specifically, the results from the MSFC field-scale application of BTS are positive despite the fact that our objective of reducing PCB values by 50% was not achieved. When the project’s objectives were first envisioned, the team had no analytical data suggesting that the starting PCB values in the paint at MSFC were as low as they are. The regulatory limit for PCBs is 50 mg/Kg and the starting levels at the 4696 F1 test stand were as low as 1.0 mg/Kg. Realistically, no cleanup system would be required for this structure. Notable is that this technology has the ability to lower PCB levels in structural material to less than 10 mg/Kg should the EPA change the regulatory allowable limit sometime in the future. Application of BTS to the stand and statistically defensible evidence suggesting 29-33% PCB removal at extremely low starting concentrations indicates the wide application-range for BTS. At these lower levels, the concentration gradient driving the transport of PCBs from hardened, weathered paint into the reactive solvent system is limited at best, and to see consistent lowering of PCB levels with multiple BTS formulation is considered extremely favorable to this technology. Furthermore, with the low initial PCB levels in the paint at MSFC, determining the percent degradation or breakdown of the PCBs removed by the BTS was not analytically feasible. Therefore, PCB degradation studies will need to be conducted in future field studies with structures containing higher levels of PCBs in the paint.

The use of BTS to remove and degrade PCBs offers NASA the opportunity not formerly envisioned with respect to its future environmental liability. In some instances, facility demolition and placement of the structure in an on-site or off-site landfill is the current leading candidate for handling structural material containing PCBs. This disposal option most certainly leads to future environmental liability with an undeclared price tag. The ability to remove and degrade PCBs without future economic investments decades down the road is itself an appealing option for both government and private entities alike. BTS potentially offers NASA that security. It also transmits a “pro-active” message to the public by treating and degrading the contaminant now, as opposed to shuffling the problem to a later generation. BTS also may offer the government a method to preserve and protect national historic monuments that contain PCBs within structural paints, caulking or binding materials.

REFERENCES


